Chapter 3

Fast Gas Chromatography:

Theoretical considerations

3.1 Introduction

Despite the tremendous decrease in analysis time that is possible with modern equipment, limited useful applications have been found for fast gas chromatography. Most often separation efficiency is sacrificed for a shorter run time. While shorter analysis times are desirable, the concurrent increase in complexity of instrumentation is unfortunate. Special low volume detectors and injectors[1] that are capable of producing very short injection bandwidths are required. Often the chromatographic run is a small part of the analysis scheme where much larger time expenses are made in sample preparation and data analysis. Thus it is not always wise to invest in new, complicated equipment when other factors dominate the total analysis and reporting time.

In the case of comprehensive multidimensional chromatography it is, however, paramount that the second separation should occur as fast as possible, since every 2nd dimension chromatogram is repeated many times. Any increase in 2nd dimension runtime is multiplied hundreds of times for each analysis. For a given 1st dimension runtime, the analysis of the 2nd dimension should also be fast enough to allow a great number of these to maintain the resolution of the 1st.

Normally fast GC alone is ineffective for detailed analysis of complex mixtures due to the limited peak capacity that can be generated. Because of the first separation, each transfer to the second column contains only a few compounds that can more readily be separated with the limited separation efficiency attainable with fast analysis.

Comprehensive multidimensional chromatography is thus an ideal application for very fast gas chromatography.

Retention mechanisms in gas chromatography are always dominated by volatility. There is an approximate exponential relationship between retention time and solute boiling point under isothermal GC conditions. When an intermediate temperature is chosen, the chromatogram is characterized by poor separation of early eluting compounds, a long analysis time and poor detectability of late eluting peaks due to band broadening. This is commonly referred to as *the general elution problem*. For mixtures of analytes exceeding a boiling point range of 100°C it is impossible to find a suitable analysis temperature. For these samples only programmed modes can achieve complete separation in good time. Both flow and temperature programming can be used. While linear temperature programming is most often used due to simpler experimental implementation, exponential flow programming offers many of the same advantages[2]. There is a small chance that with modern electronic pressure control, flow programming may gain some popularity. However, with these instruments flow rates are still calculated and the accuracy depends on the precision to which column dimensions can be defined. Efficiency is sacrificed, as columns are used at optimum flow rates only for a short period during each run. Flow programming will never be able to cover the same wide spread in volatility as temperature programming.

Negative thermal gradients in distance have been applied to chromatographic columns as a form of moving focusing[3]. Cryogenic and retention gap focusing are usually single events before or on the head of the column. With negative thermal gradients across the length of the column the zones are continuously focused as they move towards the column exit while separation takes place. Because the inlet side of the column is at a higher temperature than the detector side, the rear of the band is at a higher temperature than the front and thus moves at a slightly higher velocity. This counteracts some of the chromatographic band spreading.

Unfortunately the same forces that make the zones narrower also move the zones closer together reducing the separation because the trailing zone is at a higher temperature than

the leading zone[4]. While it can be helpful in reducing the effects of non-ideal chromatographic conditions, gradient focusing can not increase resolution or speed of analyses beyond what is theoretically achievable with conventional temperature programmed analysis (PTGC) without gradient focusing[5].

In comprehensive 2D gas chromatography, samples are first separated according to boiling point. Since all analytes in a specific transfer have the same volatility, isothermal chromatography can be used very successfully in the 2nd dimension. However, in our proposed comprehensive 2D SFCxGC the chemical class separation precedes the boiling point analysis and each subsequent transfer contains a wide boiling point range. It is therefore required that a wide boiling point range be analyzed in a very short time.
To this end, the theory behind fast gas chromatography, especially that pertaining to programmed temperature analysis, is explored in this chapter.

3.2 Optimization of resolution for fast gas chromatography

The relation between the different chromatographic variables is demonstrated by the well-known resolution equation:

$$R = \frac{\sqrt{N}}{4} * \frac{k'}{k'+1} * \frac{\alpha - 1}{\alpha} \qquad \text{[eq 3-1]}$$

where R_s is the resolution between two successive peaks, k' is the capacity factor of the most retained compound and $\alpha = k'_2/k'_1$ is the relative retention (also known as the selectivity).
The capacity factor is dependent on temperature through the thermodynamic partition coefficient, K, and the phase ratio,β.

$K=\beta k'$ [eq 3-2]

where

$\beta = Vm/Vs$ [eq 3-3]

with

Vm as the volume of the mobile phase

Vs is the volume of the stationary phase

and

$$K \propto e^{\frac{-\Delta\mu}{RT}} \qquad \text{[eq 3-4]}$$

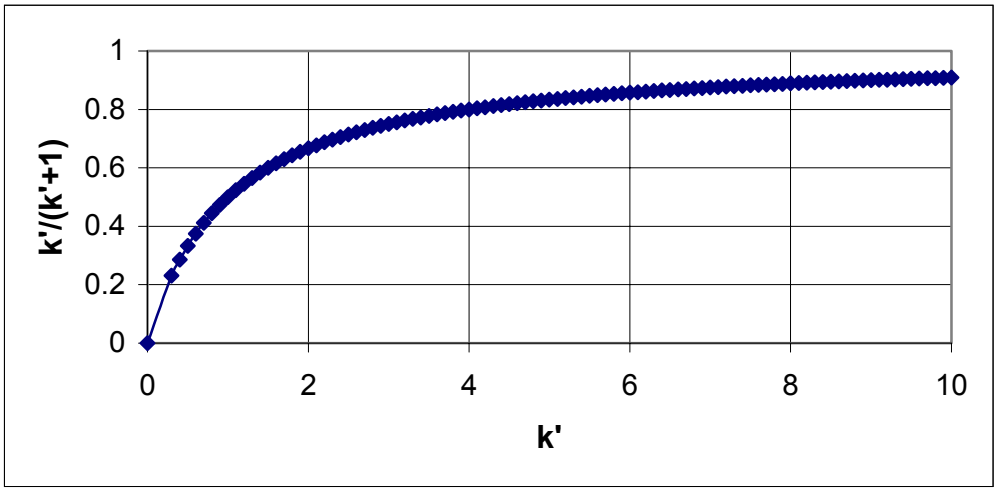
with

$\Delta\mu$ as the change in free energy.

Thus, according to equation 3-2 and 3-4 an increase in temperature will reduce the capacity factor, resulting in a decrease in resolution (through equation 3-1) as well as analysis time (equation 3-14).

For maximum resolution, conditions are chosen where the term [k'/(k'+1)] in equation 3-1 approaches the maximum value. For large retention values this term approach 1.

Figure 3- 1: **The maximum of the [k'/(k'+1)] term.**



Resolution is measured experimentally from a chromatogram as

$$R = \frac{tr_2 - tr_1}{4\sigma} \qquad \text{[eq 3-5]}$$

A resolution of R>1 implies that the retention maxima of the two compounds differ more than the band broadening of the zone in time units. This is normally expressed in terms of

the standard deviation (σ). For a peak showing a gausian profile, R=1 implies that the difference in retention time is equal to the width of the peak at base (Δtr = 4σ).
The width of a peak is influenced by non-chromatographic factors such as the introduction width and by band broadening caused during the chromatographic process. The relative band broadening is expressed in terms of the theoretical plate height, H[7].

$$H = L\frac{\sigma^2}{t_r^2} \qquad \text{[eq3-6]}$$

The relationship between H and u (the average linear velocity) for open tubular columns is given by the Gollay-Giddings equation[6]:

$$H = \left[\frac{2D_m}{u}\right] f_1 + \left[\frac{\left(1+6k'+11k'^2\right)}{96\left(1+k'\right)^2}\frac{r_c^2}{D_m}\right] f_1\, u + \left[\frac{2}{3}\frac{k'}{\left(1+k'\right)^2}\frac{d_f^2}{D_s}\right] f_2 u \qquad \text{[eq3-7]}$$

Where
D_m= diffusion of solutes in the mobile phase and
D_s= diffusion of solutes into the stationary phase.

- $$f_1 = \frac{9}{8}\frac{\left(P^4-1\right)\left(P^2-1\right)}{\left(P^3-1\right)^2} \qquad \text{[eq3-8]}$$

- $$f_2 = \frac{3}{2}\frac{\left(P^2-1\right)}{\left(P^3-1\right)} \qquad \text{[eq3-9]}$$

P = p_i / p_o (the ratio between the column inlet and outlet pressures)

This can be simplified to

$$H = \frac{B}{u} + C_m u + C_s u \qquad \text{[eq3-10]}$$

where		*represents*
-	$B = 2D_m$	longitudinal diffusion
-	$C_m = F(k)\frac{rc^2}{D_m} f_1 u$	resistance to mass transfer in mobile phase

- $C_s = \frac{2}{3}\left(\frac{k'}{(k'+1)^2}\right)\frac{D_f^2}{D_s} f_2 u$ resistance to mass transfer in stationary phase

and

- $F(k') = \frac{\left(1+6k'+11k'^2\right)}{96(1+k')^2}$ [eq3-11]

A graphical presentation of plate height against linear flow rate is known as the Van Deemter curve. Figure 3-2 is a calculated curve for hydrogen and a thin film 0.25mm capillary column. It graphically demonstrates the additive effect of B, C_m and C_s as described by equation 3-8. For thin film columns the effect of diffusion into the stationary phase is usually negligible. The value of D_s is assumed to be $3.3 \times 10^{-6} cm^{-2}.s^{-1}$ at 85°C and the value of D_m is assumed to be $0.2 cm^2/s$ for hydrogen .

Figure 3-2: Calculated Van Deemter curve

$D_s=3.3 \times 10^{-6} cm^{-2}.s^{-1}$ (at 85°C), $d_f=1 \times 10^{-4}$cm dimethyl silicone

$D_m=0.2 cm^2/s$ (hydrogen), k'=10, $r_c=0.0125$cm.

Differentiation of equation 3-8 with respect to mobile phase velocity, followed by setting the result to zero, leads to an optimum mobile phase velocity with a corresponding minimum in plate height[6].

$$u_{opt} = \sqrt{\frac{B}{(C_m + C_s)}} \quad \approx D_m/r_c \qquad \text{[eq3-12]}$$

$$H_{\min} = 2\sqrt{B(C_m + C_s)} \quad \approx d_c \qquad \text{[eq3-13]}$$

The highest column efficiency will be obtained at u_{opt}.

After separation between compounds is effected, minimization of analysis time of the separation problem is of interest.

3.3 Optimization of separation speed [6,7]

Retention in chromatography is described by[6]:

$$t_r = \frac{L}{u}(1 + k') = N(1 + k')\frac{H}{u} \qquad \text{[eq3-14]}$$

or, since the number of theoretical plates (N) attainable with a column is defined as the column length (L) divided by the theoretical plate height (H)

$N = L/H$ [eq3-15],

Retention can thus also be described as

$t_r = N(1+k')H/u$ [eq3-16]

where the flow rate is defined as

$u = L/t_m$ [eq3-17]

Retention times can be reduced at will, by reducing L or k' or increasing u. However, changing any of these parameters has a pronounced effect on the resolution between the compounds of interest. The possibilities for increasing speed of analysis for a given separation problem is limited by the relationship between retention time, column resolution and plate number.

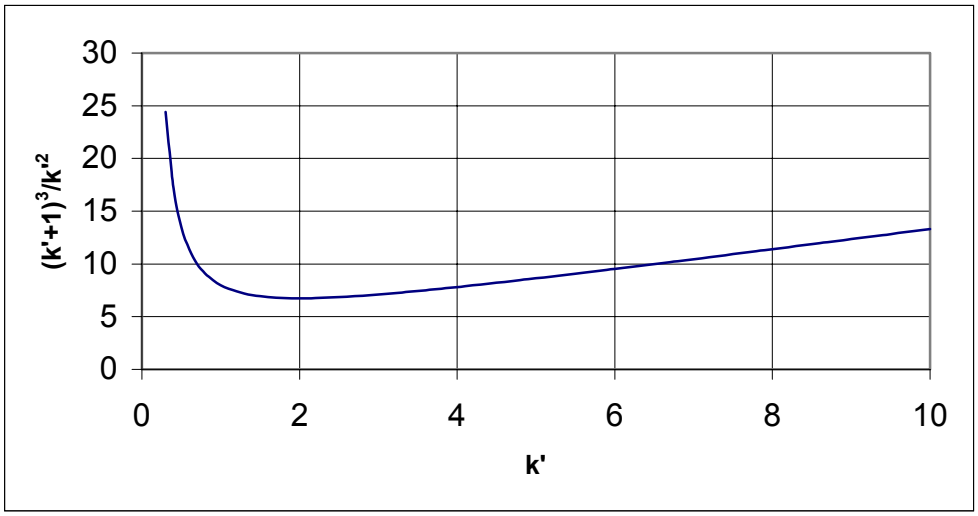
When equation 3-16 is combined with the resolution equation (equation 3-1) an equation is obtained that relates retention time with resolution. If t_r is chosen as the last eluting compound then the well known equation 3-18 gives an indication of the total analysis time of a sample:

$$t_r = \frac{H}{u}\left[16\left(\frac{\alpha}{\alpha-1}\right)^2 \frac{(1+k')^3}{k'^2} R_s^2\right] \qquad \text{[eq 3-18]}$$

While column length does not feature directly in equation 3-18, it is indirectly defined by the relationship between R and N in equation 3-1. An excess of resolution should be avoided as this leads to an increase in analysis time ($t_r \propto R_s^2$). Resolution tends to increase proportionally to the square root of the number of theoretical plates. Analysis time, however, is directly proportional to the column length. Thus, increasing column length to improve resolution is time-expensive.

3.3.1 The influence of capacity factor

Figure 3-3: The minimum retention time is obtained when k'=2.



The influence on analysis time with variation in k' is graphically represented by Figure 3-3. It can be seen that the $(1+k')^3/k'^2$ term (equation 3-18) reaches a minimum at k'=2. However, it should be remembered from Figure 3-1 that the maximum resolution is

obtained for large values of k' where the k'/(k'+1) term in the resolution equation (equation 3-1) approaches 1 (Figure 3-2). At k'=2 only 2/(2+1) i.e. 66% of the maximum resolution (at higher k' values) can be obtained. The column length could be increased to counteract the loss in resolution.

$$L = \frac{16R^2}{H} \times \left(\frac{\alpha}{\alpha - 1}\right)^2 \times \left(\frac{k'+1}{k'}\right)^2 \qquad \text{[eq3-19]}$$

This equation is obtained by combining equation 3-1 and 3-15 and rearranging to solve for column length. Working at k'=2 an increase in column length of $(2+1)^2/\ 2^2$ i.e. 9/4 or 2.25 is required to achieve the same resolution as would be obtained when working with higher retention factors.

3.3.2 The influence of selectivity

When a column is used with high selectivity between the compounds of interest, resolution is easier to obtain. This generally leads to a faster analysis as shorter columns or smaller k values can be used to obtain the required resolution. In gas chromatography high values of selectivity are generally only obtained for compounds that differ widely in boiling point. However, it can be calculated from equation 3-1, that for a conventional capillary chromatographic column that provides about N=100 000 plates, a selectivity of only $\alpha = 1.02$ is required for $R_s=1$ with k'=2.

3.3.3 Influence of carrier gas flow rate and pressure drop

Replacing H in equation 3-18 by equation 3-7 the influence of column diameter (d_c) and carrier gas on t_r becomes apparent. H can be simplified to $B/u+C_mu$ when working with thin film open tubular columns and low pressure drop conditions ($|p_i-p_o| < 0.8p_i$). At high flow rates, where the B term reaches a minimum, $H \approx C_mu$ and the ratio H/u stays constant. Under these conditions an increase in column length can be compensated for with a proportional increase in flow rate to maintain a constant R and retention time[8]. That means doubling the column length will not lead to an increased retention time, provided the flow rate is also doubled, ensuring constant N and therefore R^2.

$$tr = F(k')\left[16R_s^2\left(\frac{\alpha}{\alpha-1}\right)^2\frac{(1+k')^3}{k'^2}\right]\frac{r_c^2}{D_m} \qquad \text{[eq3-20]}$$

When the pressure drop is high (p_i-p_o > 0.8p_i) , f_1 in equation 3-7 approximately equals 9/8 and f_2 approaches 3/(2P) . The retention time is then better described as[6]

$$t_r = F(k')\left[64R^3\left(\frac{\alpha}{(\alpha-1)^3}\right)\frac{(1+k')^4}{k'^3}\sqrt{\frac{3\eta}{p_a}}\right]\frac{r_c}{\sqrt{D_m}} \qquad \text{[eq3-21]}$$

where η is the dynamic viscosity

and p_o is the outlet pressure (normally atmospheric).

3.3.4 The influence of column radius

Following equation 3-20, the retention times increase at a rate equal to the square of the column radius ($t_r \propto r_c^2$). Thus when a column with 50 μm is used as opposed to a 250 μm column, a 25 times faster analysis can be effected. However, when a high pressure drop is present across the column, the retention time is proportional to the column radius ($t_r \propto r_c$, eq3-21) and the increase in speed is reduced to 5 times that of the wider bore.

3.3.5 The influence of diffusion coefficients

Using the kinetic model of gases[9] the diffusion coefficient can be described as

$$D = \frac{1}{3}\lambda c \qquad \text{[eq3-22]}$$

where λ is the mean free path without collision of gas molecules:

$$\lambda = \frac{kT}{\sqrt{2}\sigma p} \qquad \text{[eq3-23]}$$

σ is the collision cross section of the molecule

and c is the average speed derived from the Maxwell distribution of speeds:

$$c = \sqrt{\frac{8RT}{\pi M}} \qquad \text{[eq3-24]}$$

These equations imply that the diffusion coefficients of various gasses depend on their molecular mass and the collision cross section (σ).

Table 3-1: Collision cross sections/ nm^2

Hydrogen	0.27
Carbon Dioxide	0.52

A comparison of the molecular mass and the collision cross-sections reveals that when hydrogen is used, diffusion coefficients 9 times larger than for carbon dioxide will be obtained.
In the low pressure drop case (eq 3-20) analysis times are 9 times faster when hydrogen is used as opposed to carbon dioxide. When a high pressure drop (eq3-21) exists the influence of diffusion coefficients ($t_r \propto 1/ (D_m)^{-2}$) are less and retention times are reduced by a third.

3.3.6 The relative contributions of column diameter v/s carrier gas identity

With the proposed two-dimensional $SFCxGC_{ftp}$ the first separation will be effected with high pressure CO_2. The possibility exists that it could also serve, after depressurization, as carrier gas for the GC analysis. When the influence of the carrier gas identity is compared to the decrease in analysis time through reduction of the column inner diameter, it can be concluded that for a narrow bore capillary (50μm) with CO_2, faster results will be obtained than using a wide bore capillary (250μm) with H_2. However the combined effect of using a narrow bore capillary together with H_2 will produce the best resolution in the shortest time.

In this way, resolution between a critical pair of analytes can be optimized with isothermal GC. When resolution between the critical pair is obtained it may happen that resolution between the other interesting compounds of interest is also obtained.

3.4 Temperature programmed analysis

While temperature programmed analysis does not improve the resolution that can be obtained from a specific set of chromatographic conditions, speed and the detection limits of such chromatograms are considerably increased. It has been shown that the dependence of the analysis time on the column inner diameter for a capillary column is the same in both isothermal and temperature programmed analysis[10].

Diffusion coefficients are a function of temperature. However, it can be seen from equation 3-22 to 3-24, that the respective dependencies on temperature is the same for each of the gases. It can thus be assumed that hydrogen should also be the fastest gas for temperature programmed GC analysis. The difference in the change of viscosities for the different carrier gasses with temperature is small. This difference has been calculated to be roughly equal to 1°C over the entire temperature-programming range of several hundred degrees centigrade[11]. Thus, it seems safe to assume that the influence on runtime of diffusion coefficients should also be the same for isothermal and temperature programmed chromatographic runs.

3.4.1 Heating rates

The reduction in analysis time in temperature programmed GC analysis depends on the heating rate - the higher the rate the shorter the analysis time. Unfortunately, an increase in heating rate causes a reduction in column peak capacity. The selection of the best heating rate requires a compromise between maintaining a minimum acceptable resolution for the sample while obtaining the shortest separation time.
The argument is the exact parallel to the role of temperature and capacity ratio (k') on the separation in the case of isothermal GC. Too high heating rates imply elution of compounds at too low k' values with consequent reduction in R (see figure 3-1). Too low heating rate implies final elution of compounds at too high k' values with resultant loss in separation speed (see Figure 3-3).

As opposed to the standard goal of achieving:
Good separation of a critical pair of solutes in the shortest time;

The optimization criteria of achieving:

An adequate separation of a required number of analytes in the shortest time,

is particularly useful for the general optimization of the proposed multidimensional application of fast GC. The required number of analytes can be expressed through the peak capacity (n). The analysis time of the sample (t_a) is taken as the elution time of the last eluting sample component. Blumberg[12] defined certain constraints relating to different pressure drop scenarios and obtained an optimum ramp rate (R_t) for each of the different conditions. These optima were expressed in unit temperature increase per void time (t_m). Void time is the time it takes for an unretained compound to elute from a chromatographic column.

$$r = R_t \times t_m \qquad \text{[eq3-14]}$$

3.4.2 Normalized heating rates

The concept of normalized heating rate (r) substantially simplifies the optimization of the heating rate by reducing the range of possible values that represent the heating rate. Once an optimum heating rate has been experimentally found for a particular method, there is no need to make another set of experiments to find an optimum heating rate for each set of column dimensions, carrier gas, gas flow rate, outlet pressure or any other combination of translatable changes. Translatable variations allow one to change the heating rate without moving from the optimal normalized heating rate.

3.4.3 Default Optimum Heating Rate

Based on experimental data, Blumberg recommended that for columns with silicone stationary phases with $\beta \approx 250$ (the thin film case, $C_s \approx 0$) the optimum normalized heating rate is $10°C/t_m$. Low pressure drop conditions require a factor 2 higher and an increase of 12% is suggested for every factor 2 increase in film thickness.

Table 3-2: Heating rate (°C/min) vs. column dimensions for H_2 at 10°C/tm[13]

Length /m	Diameter/ μm			
	50	100	250	320
1	1200	1200	620	490
5	110	140	110	90
10	40	53	51	44
25	10	14	17	16

As can be seen from Table 3-2 for shorter columns, the heating rate (R_T) is impossible with standard commercial gas chromatographs. For these high-speed separations, alternative methods of column heating are required. The major limitation on heating rates attainable with conventional stirred bath ovens is the huge thermal mass of the oven that needs to be heated together with the column. Modern methods provide heat directly to the small thermal mass of the capillary column. Very high heating rates up to 1200°C/min or more can be achieved. Some of the methods for obtaining these fast heating-rates will now be discussed.

3.5 Achieving fast heating rates

3.5.1 Resistive heating

Resistive heating has been applied successfully to direct heating of capillary columns. It is achieved by applying a voltage drop across a capillary that has been made electrically conductive. The increase in column temperature depends on the amount of power dissipated. The dissipated power (W) depends on the current (I) through and the voltage (V) across the column.

$$W = V I \qquad \text{[eq 3-15]}$$

The current is dependent on the voltage drop and the resistance (R) of the column.

$$I = V / R \qquad \text{[eq 3-16]}$$

The electrical resistance is dependent on the length, diameter wall thickness and composition of the electrically conductive column or conductive layer.
The amount of heat required for increasing the temperature of any substance by an increment ΔT is given by[14]

$$Q = mC\Delta T \qquad \text{[eq 3-17]}$$

Where Q is the heat (Joules or Watt·seconds), m is the mass of the material (gram), C is the heat capacity of the material(J/g.C°) and ΔT is the change in temperature of the material. Eq 3-17 demonstrates that objects with large mass require more heat or power to reach the same temperature in a given time period than an object of smaller mass. The low thermal mass of a capillary column allows it to be rapidly heated while using much less power than is normally required with a GC oven. Even more important, low thermal mass allows for faster cooling and thus cycle times.

Methods of making columns electrically conductive

Resistive heating of flexible fused silica columns with metal cladding was first suggested by Lee in 1984[15]. The first practical demonstration of this technology for GC analysis was by Hail and Yost[16] who used a short section of a commercial aluminum clad fused silica column. A programmable DC power supply was used to regulate the voltage across the column. The power supply output was regulated through a 0-5V signal derived from a digital to analog board.
Philips and Jain painted fused silica columns with a thin layer of electrically conductive paint and regulated the output from a programmable DC power supply in a similar way[17]. Mechanical instability due to differences between the thermal expansion coefficients of the fused silica and the coatings caused rupture of the conductive layer. This was further accelerated by local hot and cold spots caused by uneven coating. Chromatographic efficiency was degraded and the analytical column was damaged.
Mechanical stability was improved by Ehrmann et al[18]. They compared the use of a coaxial metal tube or collinear heater wire as an at-column heating element. Both approaches proved to be satisfactory, but the coaxial heater provided better retention time

reproducibility. The tubular design allowed the use of an auxiliary sheath gas to even out heat distribution along the column. While this gas had a statistically significant advantageous effect, the benefit was too small to justify the additional instrumental complexity. A pulse width modulator operating at 100Hz was used to control the temperature.

An instrument using a coaxial heater is commercially available. The Flash-GC[19] embodies a conventional 0.25mm id column, either 6 or 12 meters long, placed inside a precision-engineered metal tube. The tube can be heated up to 1200°C/min but was sold in 2001 for approx. £20 000 pounds.

3.5.2 Microwave Heating

A recent commercial development uses a modified exterior polyimide coating that absorbs microwave radiation. The column is placed in a cell that can be installed into a traditional GC. With the microwave generator turned on, the column can be heated at rates up to 600°C/min. It takes about 60 seconds for the column to cool down to starting temperature, resulting in a typical cycle time of 180 seconds. Resolution and repeatability is claimed to rival conventional GC[20].

Induction or infrared heating could potentially be used for heating of the column.

3.5.3 Methods of sensing temperature

In the beginning, resistive heating was calibrated through an iterative process where the heating profile was changed until the desired normal paraffin separation was obtained[17]. This time consuming process was not very flexible and discouraged the changing of ramp rates. The actual column temperature and heating rates were also unknown.

Thermocouples could be considered impractical for this application due to their relatively large thermal mass in comparison to the capillary column wall onto which they are to be connected. Even if small sensors were placed on the column, local cold spots would be caused and this may lead to inaccurate temperature measurements, possibly producing peak tailing due to local cooling.

3.5.3.1 Resistance measurements

It was opted instead to use the resistance of the conductive capillary column as an indication of the average temperature[17]. The resistance of any metallic conductor is linearly related to its temperature over a large temperature range and is given by:

$$R_T = R_o(1 + \alpha T) \qquad \text{[eq3-18]}$$

Where R_T is the resistance at T, R_o is the resistance at 0°C and α is the temperature coefficient of resistivity of the metal. The simplest way to measure the resistance is to calculate it from the current through, and the voltage drop across, the column:

$$R = V / I \qquad \text{[eq3-19]}$$

Since the current through every point of a circuit is the same, the current through a high Wattage, low resistance, resistor in series with the column can be measured by measuring the voltage drop across this known and constant resistor. This was the approach followed by Hail and Yost[16].

The resistance of the column was calibrated against known temperatures and used as a direct measure of temperature.

3.5.3.2 Resistance measurement with superimposed AC signal

Philips measured the resistance of the column by superimposing a supposedly constant current 10kHz square wave on top of the DC heating current. The square wave was sampled at 20kHz and the amplitude of this voltage measurement was proportional to the resistance and hence the temperature of the column[17].

This circuit (Figure 4-2) was somewhat delicate and required empirical tuning to obtain good results. Very small signals of about 10 to 20mV had to be measured at high frequency. Electronic noise is definitely a problem in a laboratory environment with lots of electronic equipment. Despite the incorporated band pass filters, noise equal to 10°C can be discerned from the published graphic results.

3.5.3.3 Separate sensing wire

With the column-in-a-sleeve design by Ermann[18] it was also possible to incorporate a separate sensor wire. A small constant sensing current was passed through the wire. The resultant voltage drop across the wire is proportional to the resistance of the wire (eq 3-19) and this resistance is proportional through equation 3-18 to the temperature.

3.5.3.4 Infrared temperature sensing

Infra red temperature sensors are excellent non-contact sensors and thus do not cause cold spots. They are available in models that offer much the same temperature range and linearity as type K thermocouples. However, even with close focusing optics the smallest measurement spot size of commercial models are 2.5mm^2. This is many times bigger than the surface of a capillary column. A couple of column windings could potentially be coiled tightly together but each coil would have to be electrically insulated from its neighbors and this will increase thermal mass and cool down times.

3.5.4 Temperature Control[21,22]

In order to do useful gas chromatography it is necessary to accurately and reproducibly control the temperature. Isothermal temperatures should be well maintained and temperature ramps promptly and precisely followed. This implies that the temperature should be constantly monitored and control variables need to be continuously altered as the set-point changes or when the measured temperature is different from the set point. The process where a measurement is compared with a set point before corrective action is taken is called feedback control. The difference between the set point (SP) and the measured signal, also called the process variable, (PV) is the error(e)

$$e = SP - PV \qquad \text{[eq 3-20]}$$

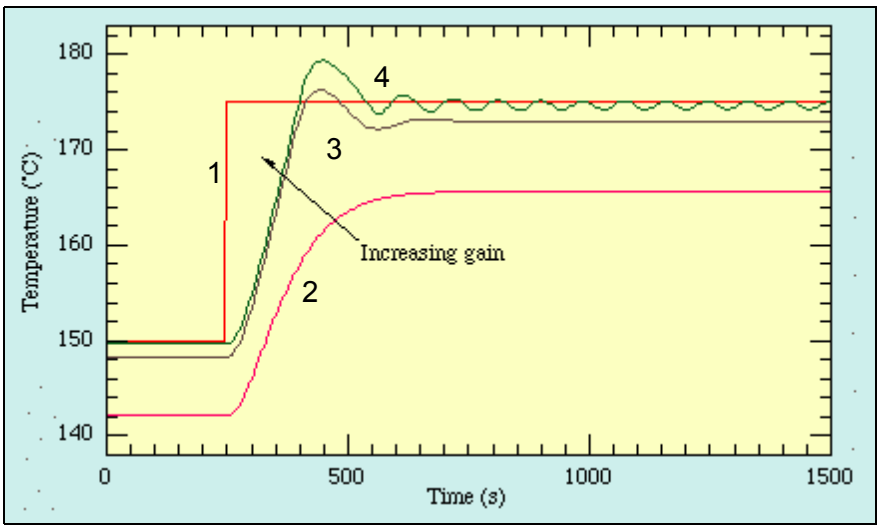
3.5.4.1 The proportional controller

A proportional controller attempts to apply power, W, to the heater in proportion to the size of the error, where P is known as the proportional gain of the controller:

$$W = P\ e \qquad \text{[eq 3-21]}$$

As the gain is increased, the system responds faster to changes in set point and may eventually start to oscillate as the controller becomes unstable. When a small proportionality constant is chosen (Figure 3-2 no.2) the final oven temperature after a step function disturbance (Figure3-2 no.1) lies below the set point because the product of the error and proportionality constant is too low to request adequate power from the heater. Increasing the gain alleviates this problem but at very high gain the process variable may overshoot and start to oscillate around the set point (Figure 3-2 no.4).

Figure 3-2: Proportional control



1. A step increase in temperature of set point.
2,3. Increasing the gain (P) causes faster response to set point changes
4. At very high gain, temperature (PV) oscillate around control value (SP).

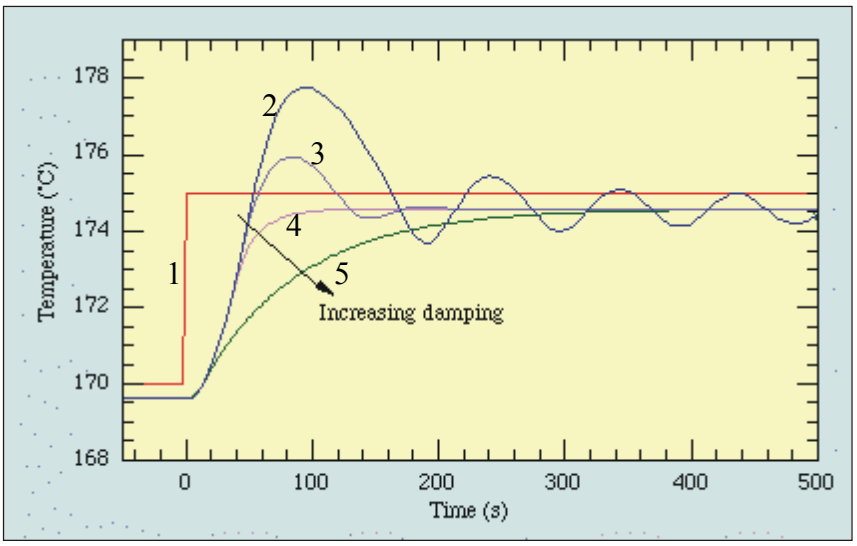
3.5.4.2 Proportional+Derivative Control

Adding the time-derivative of the error signal to the control output can improve the stability and overshoot problems that arise when a proportional controller is used at high gain:

$$W = P\left(e + D\frac{d}{dt}e\right) \qquad \text{[eq 3-22]}$$

This technique is known as PD control. The value of the damping constant, D, can be adjusted to achieve a critically damped response to changes in the set-point temperature, as shown in Figure 3-3. Too little damping results in overshoot and ringing (Figure 3-3 no.2), too much cause an unnecessarily slow response (Figure 3-3 no5).

Figure 3-3: PD control



1. Set point with step increase in temperature
2. High gain causes 'ringing' of process variable

3-5. Increasing damping improves oscillations

3.5.4.3 Proportional+Integral+Derivative Control

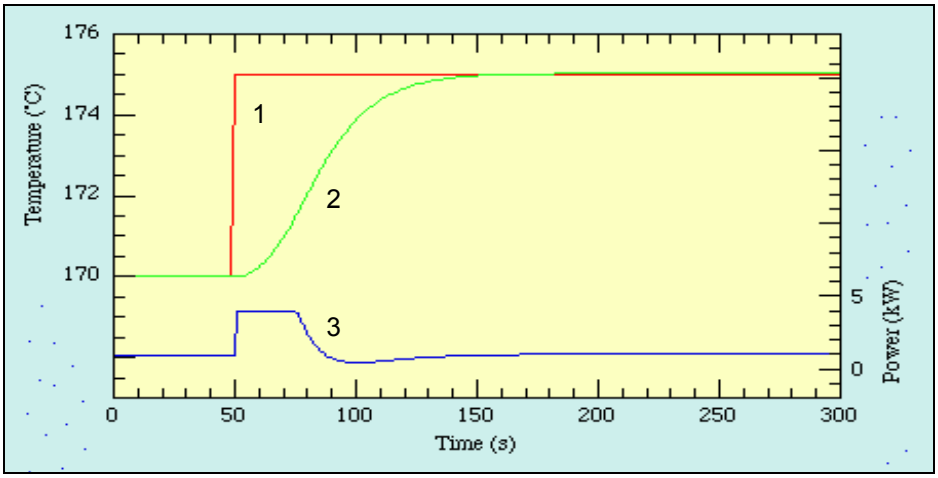
Although PD control corrects the overshoot and ringing problems associated with proportional control, it does not cure the offset problem encountered when a small gain is used. Fortunately, it is possible to eliminate this steady-state error while using relatively low gain by adding an integral term to the control function, which becomes:

$$W = P \times \left(e + D\frac{d}{dt}e + I\int e dt \right) \qquad \text{[eq 3-23]}$$

Here, I, the integral gain parameter is sometimes known as the controller reset level. This form of function is known as proportional-integral-differential, or PID, control. The

effect of the integral term is to change the heater power until the time-averaged value of the temperature error is zero. The method works quite well but complicates the mathematical analysis slightly because the system is now third-order.

Figure 3-4: PID Control



1. Step increase in set point.
2. Process variable (temperature) follows set point.
3. Controller output.

Figure 3-4 shows that, as expected, adding the integral term has eliminated the steady-state error.

3.5.4.4 Proportional+Integral Control

Sometimes, particularly when the sensor measuring the oven temperature is susceptible to noise or other electrical interference, derivative action can cause the heater power to fluctuate wildly. In these circumstances it is better to use a PI controller or set the derivative action of a PID controller to zero. When a ramp as opposed to a step function is used to set the temperature, derivative action is often not required.

3.5.5 The Control variable

For resistive heating there are two control possibilities:

1. A continuous current can be increased or decreased depending on the size of the error signal
2. or a fixed current output can be turned on and off for various lengths of time in response to the error signal. The latter case is called pulse width modulation (PWM).

3.6 Chapter conclusion

Temperature programming of the chromatographic column is required for the separation of the wide boiling point range of samples with the 2nd dimension of the SFCxGC$_{ftp}$. Fast heating rates are required, because of the limited time available for the 2nd dimension analysis. Resistive heating is a well-established technique for fast heating of capillaries. While commercial resistive heating instrumentation is available, when attempting to duplicate such a system, the various methods of temperature sensing should be compared.

Chapter 3

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